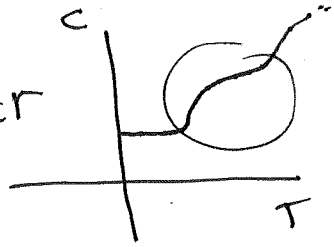
Astronomy night (SES) 7:45pm Physics

Quiz 4 today

Quiz 5 will be on Thursday, April 7

Today's goals:



(1) Understand heat capacity of rotating heteronuclear diatomic molecules like HCl, CO

(2) Application of Boltzmann statistics to systems with continuously varying energy states

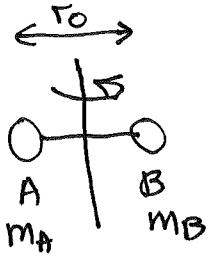
(a) equipartition theorem

(b) Maxwell-Boltzmann speed distribution

(c) classical electric and magnetic dipoles

Reading: 6.3-6.5, indicated parts of Chapter 5 (needed for Sections 6.5, 6.7)

Heat capacity $C(T)$ for rotating heteronuclear diatomic molecules like HCl, CO



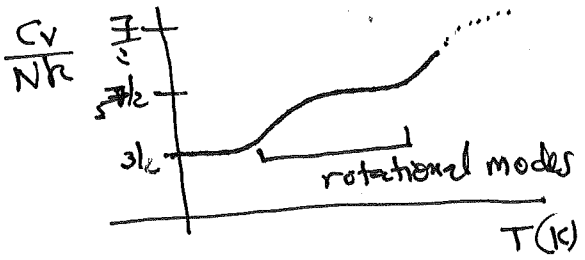


Fig 1.13 on p.30 of Schroeder

Assume ideal gas of identical diatomic molecules (so gas has high temperature, low density $\Rightarrow$ particles don't interact)

Quantum mechanics tells us the energy values E_n and their degeneracies d_n:

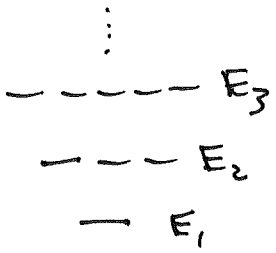
$$E_n = n(n+1)\epsilon$$

$$d_n = 2n+1$$

$$n = 0, 1, 2, \cdots$$

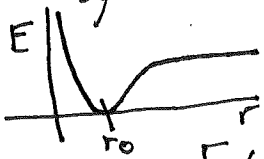
$$\epsilon = \frac{\hbar^2}{2\mu_{AB} r_0^2} \qquad \mu_{AB} = \frac{1}{\frac{1}{m_A} + \frac{1}{m_B}}$$

(reduced mass)



r_0 = equil distance between A and B

$$H\psi = \frac{L^2}{2\mu}\psi = E\psi$$



We conclude:

$$Z = \sum_s e^{-\beta E_s} = \sum_n d_n e^{-\beta E_n} = \sum_{n=0}^{\infty} (2n+1) e^{-\beta[n(n+1)\epsilon]}$$

$\sum_s$: sum over all states

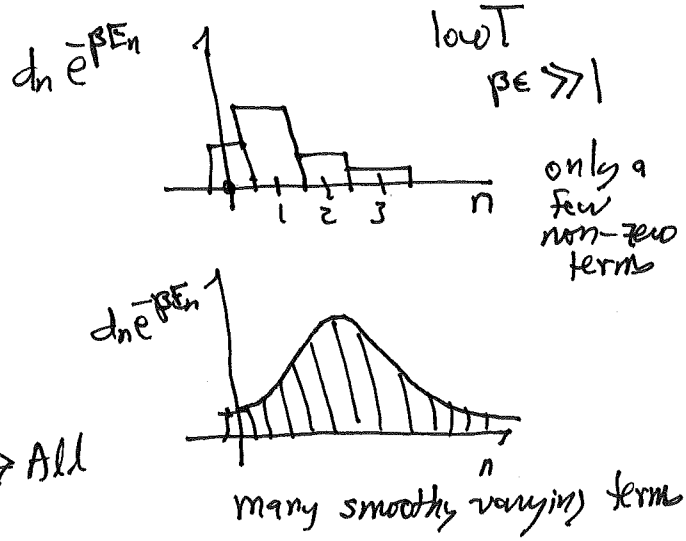
$\sum_n$: sum over distinct energies

No analytical simplification is known for general temps T, although there is a simplification for large T, when equipartition approximately holds

High-Temperature Behavior of Rotating Diatomic Molecules

Mathematica code that evaluates terms $d_n e^{-\beta E_n}$ in partition fn gives some insights about how to approx Z when T is large ($kT \gg \epsilon$):

```
ListPlot[
  Table[
    (2n+1) Exp[-n(n+1) β ϵ],
    {n, 0, 20}
  ],
  Filling → Axis, PlotRange → All
]
```



Recall that, as $T \to 0$, $Z \to 1$, just a few terms in the sum

$T \to \infty$, $Z \to N$, many terms in sum

For many diatomic molecules, turns out that

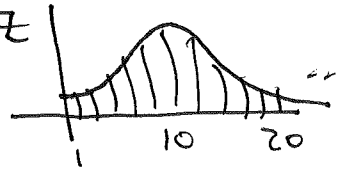
$$\epsilon \simeq 10^{-4}\ \text{eV} \equiv T \simeq 10^{-4}\ \text{eV} \times \frac{12{,}000}{1\ \text{eV}} \simeq 1\ \text{K}$$

so room temperature 300K is high-temperature regime for most diatomic molecules and Z has many terms, of order 100 or so.

(next)

Fact that, at room temp $T \sim 300\,K$, Z has many slowly varying terms suggests strategy of approximating sum by integral:

$$\sum_{n=0}^{\infty} d_n e^{-\beta E_n} \simeq \int_0^{\infty} d(n)\, e^{-\beta E(n)}\, dn$$



Fortunately, we end up with simple integral:

$$Z_{rotational} = \sum_{n=0}^{\infty} (2n+1)\, e^{-\beta \epsilon n(n+1)} \simeq \int_0^{\infty} (2n+1)\, e^{-\beta \epsilon n(n+1)}\, dn$$

$u = \beta \epsilon n(n+1)$

$du = \beta \epsilon (2n+1)\, dn$

$$= \int_0^{\infty} e^{-u} \cdot \underbrace{\left(\frac{du}{\beta \epsilon}\right)}_{=(2n+1)\,dn} = \frac{1}{\beta \epsilon} = \frac{kT}{\epsilon}$$

So for high temperatures,

$$Z \simeq \frac{kT}{\epsilon} \Rightarrow \langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{1}{(kT/\epsilon)} \cdot \left(\frac{-k^2T^2}{\epsilon}\right)$$

$$= kT \quad \text{provided } kT \gg \epsilon$$

therefore

$$\boxed{U = N\langle E \rangle = NkT}$$

, this is equipartition theorem result with $f = 2$ degrees of freedom

$$C_{rot} = \frac{dU}{dT} = Nk = N \cdot 2 \cdot \left(\frac{kT}{2}\right)$$

$\uparrow$

$f = 2$

Low-temperature behavior of heat capacity from low-temperature behavior of partition $f^n Z$

Can also get some analytical insight about low-T behavior of heat capacity of rotational part of diatomic molecules using general argument for any partition f^n. I claim that, for sufficiently low temperatures T,

$$\boxed{Z \simeq 1 + d_2 e^{-\beta E_2}}, \quad \text{low-T approx}$$

the partition f^n can be approximated by the first two terms of the possibly infinitely many terms

$$Z = 1 + d_2 e^{-\beta E_2} + d_3 e^{-\beta E_3} + \cdots$$

Reason is that if we order energies by their distinct values

$$E_1 = 0 < E_2 < E_3 < \cdots \qquad E_n \text{ has degeneracy } d_n$$

then $$e^{-\beta E_n} / e^{-\beta E_m} = e^{-\beta(E_n - E_m)} \ll 1 \qquad \begin{matrix} T \text{ small} \\ E_n > E_m \end{matrix}$$

if T is tiny, β is big; if $n > m$, $E_n - E_m > 0$ so $\beta(E_n - E_m)$ is big so $e^{-\beta(E_n - E_m)}$ is extremely tiny, i.e. $d_3 e^{-\beta E_3}$ is negligible compared to $e^{-\beta E_2}$, etc.

So $Z \simeq 1 + d_2 e^{-\beta E_2} \Rightarrow \boxed{\ln Z = \ln\left(1 + d_2 e^{-\beta E_2}\right) \simeq d_2 e^{-\beta E_2}}$

since, for T small, βE_2 large, $d_2 e^{-\beta E_2} \ll 1$.

Low-T Heat Capacity Continued

Then: $\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} \leftarrow -\frac{\partial}{\partial \beta}\left[d_2 e^{-\beta E_2}\right]$

$= d_2 E_2 e^{-\beta E_2}$

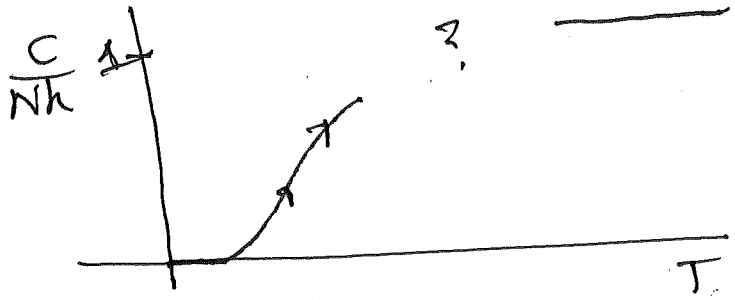
and so $U = N\langle E \rangle = N d_2 E_2 e^{-\beta E_2} = N d_2 E_2 e^{-E_2/(kT)}$

and you can show

$$C = \frac{dU}{dT} = Nk \cdot d_2 \cdot \left(\frac{E_2}{kT}\right)^2 e^{-E_2/(kT)}$$

for small temperatures $kT \ll E_2$

So get a universal form for low-T behavior of heat capacity



For general temperatures, have to use numerical methods. With symbolic manipulator like Mathematica, especially quick and easy

$$Z = \sum_{n=0}^{N} (2n+1)\, \mathrm{Exp}\left[-\beta \epsilon n(n+1)\right]$$ evaluate symbolically

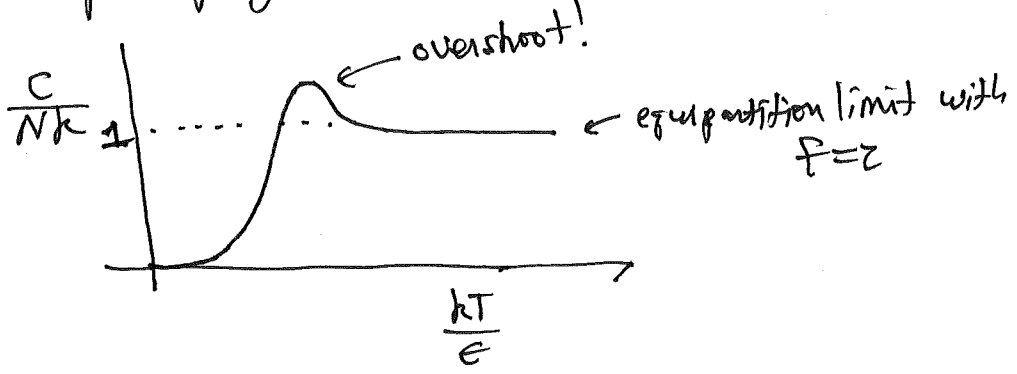
evaluate $\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$ symbolically

$C = N\frac{d\langle E \rangle}{dT}$ symbolically

See posted MMa code

rotating-heteronuclear-diatomic-molecule.nb

Show using computer projector



Get a little surprise: C does not increase monotonically as T increase, there is small overshoot leading to bump.

This is correct for heteronuclear molecules like HCl but wrong for homonuclear diatomic molecules like H_2. The latter is too subtle to explain in this course, related to fact that there are two kinds of H_2 molecules, corresponding to different spin arrangements of ~~electrons~~ protons.

See Problem 6.30 on p. 237 of Schroeder, where so-called orthohydrogen and parahydrogen states are discussed, and computation gives agreement with Fig. 1.13 of Schroeder.

See "Statistical Thermophysics" by Harry Robertson for an advanced discussion